Polymers of Intrinsic Microporosity (PIMs)

Polymers of Intrinsic Microporosity (PIMs).

Neil B. McKeown*

EaStCHEM, School of Chemistry, University of Edinburgh, David Brewster Road, Edinburgh, EH9 3FJ, UK.
E-mail: neil.mckeown@ed.ac.uk; Tel: +44 131 6504807

Abstract

Based on cumulative research from the past two decades, this personal perspective defines the structurally unique features of Polymers of Intrinsic Microporosity (PIMs), which result in a distinct combination of properties, including solution-processability and microporosity, providing organic materials suitable for the fabrication of membranes that perform efficient molecular sieving.

Highlights

- Personal reflection on the development of Polymers of Intrinsic Microporosity (PIMs).
- Explanation of why PIMs form a distinct class of polymer and microporous material.
- Re-definition of PIMs based on their method of synthesis, structure and properties.
- Rigidity and sub-nanometre pore size combine to make PIM membranes selective.
- Free volume is largely interconnected but only for the transport of small gases.

1. Introduction

Polymers of Intrinsic Microporosity (PIMs) comprise a relatively new class of macromolecule, with initial disclosure in a patent application in 2003[1] and reported in the open literature in 2004.[2] Subsequently, the synthesis, properties and applications of PIMs have been the subject of over 700 publications and 80 patents with research activity accelerating in recent years. Many comprehensive reviews of various aspects of PIM research have been published and the current perspective does not aim to provide yet another.[3-10] Instead, it will reflect on the results of these studies to provide greater clarity on what makes PIMs distinct from other macromolecules by identifying their unique structural features and distinguishing properties.

1.1. Microporous polymers. Micropores are defined by IUPAC as pores with a diameter less than 20 nm.[11] The formation of stable micropores within a polymer must overcome cohesive attraction between different chains (or neighbouring segments of the same chain) to avoid their collapse. Most polymers possess sufficient flexibility and rotational freedom to rearrange so as to maximise cohesive interactions and prevent microporosity. Therefore, despite the development of many types of macro- and mesoporous polymeric materials soon after Staudinger's definition of macromolecules was adopted in the 1920s,[12] the first well-defined polymeric *microporous* materials were reported by Davankov only in the 1970s, based on extensive crosslinking of a solvent-swollen polystyrene gel.[13] The widespread commercial exploitation of Davankov's hypercrosslinked polymers (HCPs) as adsorbents is due to their attractive combination of microporosity, low cost and ease of processing into a useful bead configuration via suspension polymerisation of the polystyrene precursor.[13] The inherent structure of hypercrosslinked network polymers, within which, formally, a network of covalent bonds links all monomeric units within the polymer to each other, provides local structural stability that is well suited for maintaining microporosity. Since the disclosure of polystyrene-based HCPs, many types of microporous network polymers have been reported based on a large diversity of bond-forming reactions and precursors. Amorphous examples include the Porous Aromatic Frameworks (PAFs)[14] and Microporous Conjugated Polymers (MCPs).[15] Of particular global interest are networks formed using reversible bond formation for which crystalline order is obtained, including the much-studied Metal-Organic-Frameworks (MOFs)[16] and the structurally related Covalent-Organic-Frameworks (COFs)[17] based on reversible covalent bond formation.

1.2. The Development of PIMs. The concept of PIMs developed from the author's research on the synthesis of phthalocyanine and porphyrin based porous network polymers as potential heterogeneous catalysts.[18] In order to stop co-facial aggregation of the large planar aromatic macrocycles, fused spirobisindane (SBI) units were used to enforce a perpendicular arrangement.[19, 20] These were introduced by dibenzodioxin formation using cheaply available 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1-spirobisindane **1**, which is the readily prepared condensation product between acetone and catechol. This strategy worked well providing catalytically active porous network polymers with apparent BET surface areas (SA_{BET}) of up to 1000 $m^2\ g^{-1}$ (Fig. 1a).[21]

In order to evaluate the efficiency of dibenzodioxin formation, biscatechol **1** was reacted with commercially available 2,3,5,6-tetrafluoroterephthalonitrile **2** to form a non-

network polymer (Fig. 2) by researcher Kadhum Msayib. The resulting yellow, highly fluorescent product proved to be a soluble polymer with a high molecular mass, as demonstrated by gel permeation chromatography (GPC) and by its formation of robust self-standing films. Surprisingly, in powder form, the polymer (eventually to be called PIM-1) demonstrated nitrogen adsorption at 77 K with significant uptake at low relative pressure suggesting that the material was predominately microporous. A description of PIM-1 and a series of related polymers, all prepared using the same dibenzodioxin formation (i.e. aromatic nucleophilic substitution), was published in a communication entitled "*Polymers of Intrinsic Microporosity (PIMs): robust, solution-processable, nanoporous materials*".[2] The immediate potential of PIMs as membrane materials was quickly understood by Peter Budd, the author's longstanding collaborator, who supervised a proof-of-concept study on using PIM-1 as a membrane for the separation of phenol from water using pervaporation.[22]

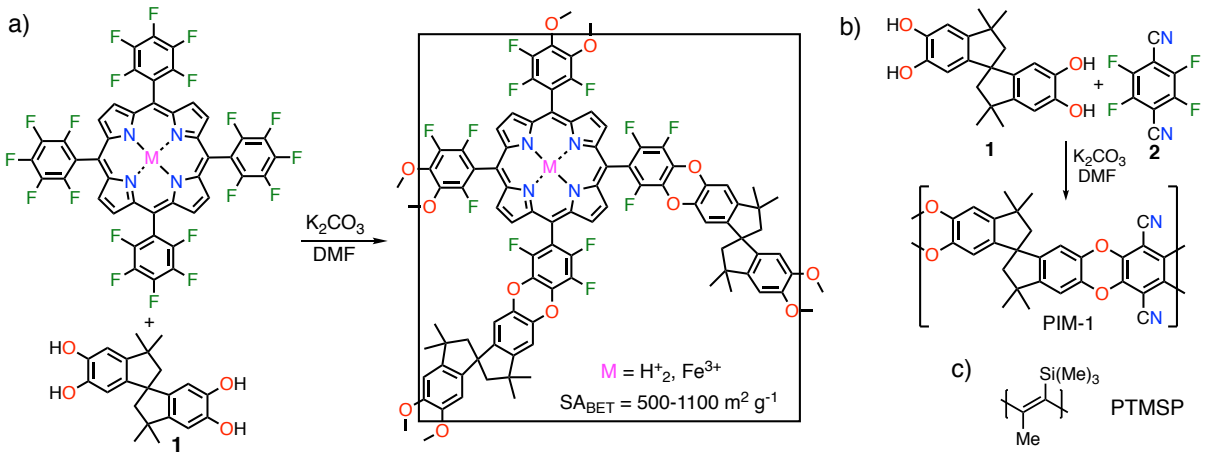

Fig. 1 (a) The synthesis of a porphyrin-based network PIM.[19] (b) The synthesis of PIM-1.[2] (c) The structure of PTMSP.

1.3. A PIM by any other name…would be a microporous polymer. The name *Polymer of Intrinsic Microporosity* (PIM) was originally coined by the author[2] in an attempt to make a clear distinction between the newly developed polybenzodioxin polymers, such as PIM-1, and high free volume polyacetylenes, such as poly(trimethylsilyl propyne) (PTMSP; Fig. 1c). PTMSP, first reported by Masuda *et al.* in 1983,[23] was the only other polymer without a network structure to be identified as a microporous material,[24] a conclusion reached due to the extraordinarily high gas permeability of its freshly cast films. Aged films of PTMSP are far less gas permeable than those that are freshly prepared, eventually losing up to 90% of the initial permeability,[25] suggesting that the microporosity of PTMSP is transient rather than an

intrinsic property of the polymer. The gas permeability of cast films of PIM-1 was not measured until 2005,[26] therefore, a direct comparison of aging between films of PIM-1 and PTMSP was not available for the 2004 communication. However, nitrogen adsorption of aged powdered samples of PIM-1 did not reduce significantly over time therefore implying, at least to the author, that its microporosity was *intrinsic* to the molecular structure of these polymers rather than relying on the history of the sample. Subsequently, it has been established that gas permeability of films of PIM-1 (and all other PIMs) also reduce on aging, in common with all glassy polymers, although at a slower rate than those of PTMSP.[27] Nevertheless, the generation of microporosity by a PIM is clearly *intrinsically* related to its macromolecular structure so that the "I" in PIM is justified. The classification of PIMs as *microporous* materials initially proved controversial, with feedback at conferences being particularly critical of the use of nitrogen isotherms to calculate a "surface area" using Brunauer-Emmett-Teller (BET) theory (Section 3.2). Similar criticisms did not appear in the literature, with the exception of scholarly analysis of the cryogenic gas adsorption of PIM-1.[28, 29] In retrospect, whilst the criticism of the widespread reporting of BET surface areas (SA_{BET}) for most classes of porous polymers is justified,[30] there is no systematic reason to exclude PIMs as microporous materials using the criteria defined by IUPAC (Section 3).[11] The acronym PIM (preferred over the initialism P. I. M.) continues to provide excellent branding for this class of polymer, perhaps benefitting from the plural "PIMs" evoking an intoxicating, British, summer drink on the patio!

1.4. Intrinsic Microporosity and Internal Molecular Free Volume. It has become clear that there is a close relationship between the concept of Intrinsic Microporosity (IM), as demonstrated by PIMs, and that of Internal Molecular Free Volume (IMFV), introduced by Swager *et al*.[31] Theoretical studies have shown that random arrangements of geometric shapes with concave faces fill space inefficiently.[32] The archetypal molecule with obvious concavities is triptycene (Fig. 2a), for which the concept of IMFV was defined as the unoccupied volume of the concavities relative to the total volume of the molecule "*swept-out by their aromatic faces*".[31] The minimisation of IMFV was exploited for the design of triptycene-based dyes that orientate in liquid crystals, due to the rod-like molecules filling the triptycene concavities, or for aligning flexible polymer chains by their interaction with triptycene cavities.[33] In addition, Swager *et al*. used IMFV as a method of generating high performance dielectric materials from enhancing free volume in various classes of

polymers.[34] Intrinsic Microporosity can be thought of as a macromolecular extrapolation of the molecular concept of IMFV, in which structural units that contain concavities are fused together so that larger elements of unoccupied free volume are generated from packing in the solid state (Fig. 2b). This process is best understood and visualised using chain packing simulations which has proved to be a very important tool for analyzing[35] and even predicting[36-38] the generation of IM in polymer solids (Section 3). Previously, PIMs have been defined as polymers that provide "*continuous network of interconnected, intermolecular voids, which form as a direct consequence of the shape and rigidity of the component macromolecules*".[39, 40] In hindsight, this appears too general and by considering both their molecular structures and properties, a more focussed definition of PIMs will be proposed in this perspective (Section 4).

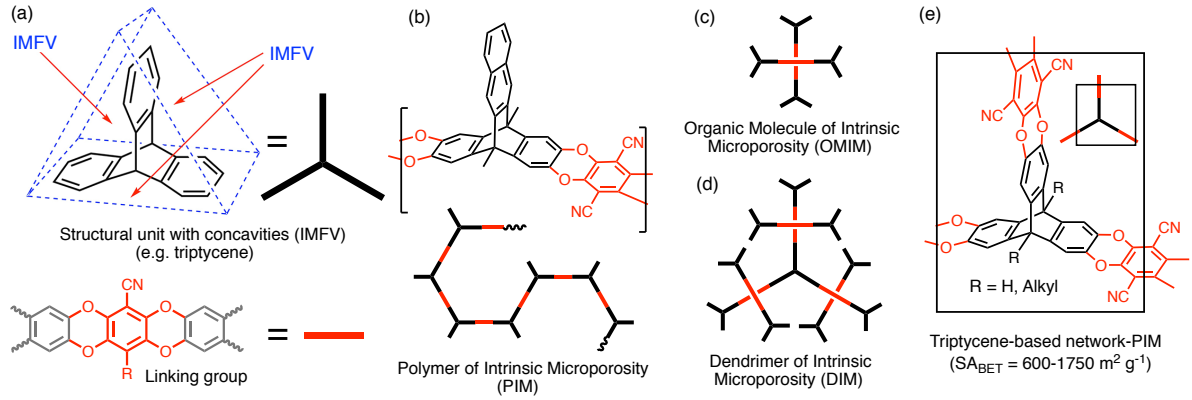

Fig. 2. (a) The concept of internal molecular free volume (IMFV) and that of intrinsic microporosity (IM) illustrated for triptycene-based PIM (b), OMIM (c), DIM (d), and Network-PIM (e).

2. Structural design rules for the generation of intrinsic microporosity.

2.1. Non-network polymers. Generally, PIMs are composed of two components: firstly, a structural unit that possesses concavities and introduces a site of contortion into the polymer chain and, secondly, a linking group (e.g. derived from dibenzodioxin or imide formation) that fuses the structural units together during polymerization but prohibits rotation of one unit relative to its neighbours (Fig. 2b and 3). To use PIM-1 as an example, the structural unit is spirobisindane (SBI), derived from monomer **1**, and the linking group is composed of a fused linear unit based on benzodioxin formation during polymerization with monomer **2**. In addition to SBI, many different structural units have been employed for making PIMs

including spirobifluorene (SBF)[41-43], for which the fused benzo groups enhance rigidity about the spiro-carbon, and highly rigid bridged bicyclic units, such as ethanoanthracene (EA)[44-47], triptycene (Trip)[48-50], benzotriptycene (BTrip)[37, 51, 52] and Tröger's base (TB). TB is a particularly versatile structural unit for PIM synthesis due to its non-linear structure and ease of formation, therefore, it can be used both as the linking group during polymerization and as the structural unit by employing a TB-containing monomer.[46, 53, 54] When employed as a linking group, the nonlinear structure of TB acts as a site of contortion so that none is required in the diamine precursor in order to obtain a PIM (e.g. making 1,4-diamino-2,5-dimethylbenzene a suitable monomer).[53] Due to these structural criteria, most PIMs have been prepared using step-growth polymerisations based on dibenzodioxin, TB or imide linking group formation. For the latter, it is important to restrain rotation about the imide N-C bond by the use of appropriate diamine monomers (e.g. 2,3,5,6-tetramethylbenzene-1,4-diamine).[47, 50, 54-57]

An additional polymerization reaction that is fully proven to yield PIMs is based on the Catalytic Arene-Norbornene AnnuLation (CANAL) for which the bridged bicyclic norbornane unit provides the site of contortion within rigid fused ring structure.[58-60] It is notable that all successful PIM preparations are via a step-growth polymerization using a reaction that involves the formation of more than one covalent bond for each monomer incorporated into the polymer. It is clear that other types of polymerization reactions, such as the Diels-Alder (DA) reaction, could be used for PIM synthesis, however, despite the synthesis of some suitable DA polymer candidates,[61, 62] their porosity has not been investigated to date.

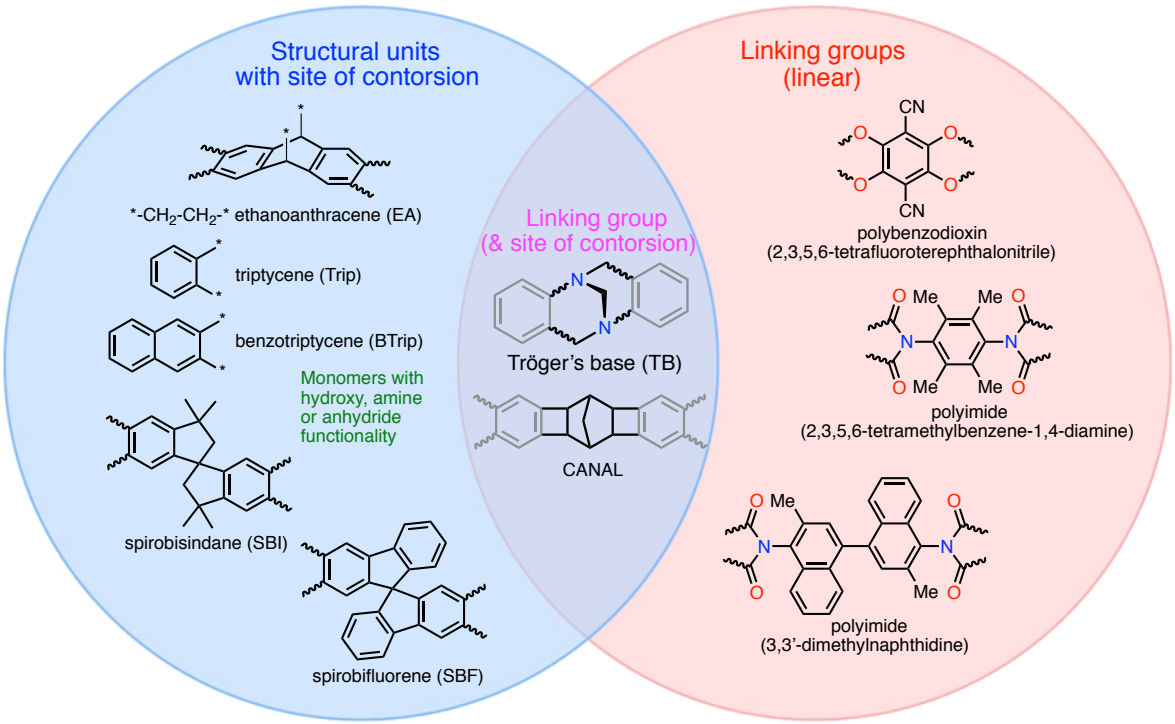

Fig. 3. PIMs are comprised of predominately fused ring chains within which structural units provide sites of contortions, to avoid linearity, with linking groups formed during the step-growth polymerisations. Tröger's base (TB) can act as both structural unit and linking group.

Post-synthetic modification of PIMs is also a useful method of tailoring properties. Most studies have focused on reactions of the nitrile group of PIM-1 to introduce carboxylic acid[63, 64], amine,[65] thioamide,[66] tetrazole[67, 68] or amidoxime[69] groups. Quaternisation of the amines in TB-based PIMs is a simple method for producing a positive charged polymer chain.[70] Most of these modifications enhance polymer cohesion and reduce microporosity but extend the structural diversity for PIMs and their potential applications.

2.2. Organic Molecules of Intrinsic Microporosity. During the early work on PIMs, it was observed that oligomeric by-products of PIM-1 gave a similar gas adsorption isotherm to that of the polymer. This observation inspired the preparation of well-defined Organic Molecules of Intrinsic Microporosity (OMIMs),[71] which involves fusing together rigid structural units with concavities, such as triptycene, using dibenzodioxin formation (Fig. 2c). Gas adsorption properties of some of these OMIMs, and that of similar oligomeric structures prepared by other groups,[72] were similar to that of PIM-1 with apparent SA_{BET} values of up to 700 $m^2 g^{-1}$.[73-75] Notably, structurally related Dendrimers of Intrinsic Microporosity (DIMs) do not show a significantly greater degree of microporosity than the OMIMs (Fig. 2d).[76] Therefore,

it can be concluded that the generation of IM is not dependent on the component molecules possessing a large molecular mass.

2.3. Network polymers. Despite the PIM concept originating from work on making porous network polymers (e.g. Fig. 1 and Fig. 2e), the identification of the role of IM in generating microporosity in polymer networks is challenging. Many network polymers, such as the long-established HCPs, and more recently developed PAFs and network polyimides are highly microporous despite lacking the key structural criteria associated with IM – i.e. in contrast to PIMs they possess linking groups that allow full rotational freedom. Therefore, can IM be identified in network polymers? Therefore, can network-PIMs be classified as a distinct subset of microporous network polymers?

For a specific network polymer, these questions might best be answered by considering the potential microporosity of an analogous non-network polymer (Fig. 4). For Davankov's HCPs, the analogous non-network polymer (i.e. polystyrene) is non-porous, therefore, is no contribution from IM to the overall microporosity. For the "Porous Aromatic Framework" termed PAF-1, of SA_{BET} = 5500 m^2 g^{-1},[14] an analogous non-network polymer could be derived from the Yamamoto coupling of di(4-bromophenyl)diphenylmethane. However such a polymer is unlikely to be microporous due to the unrestrained rotation about the biphenyl C-C bond allowing efficient packing of the chains (Fig. 4). Therefore, as for HCPs, IM does not contribute to the microporosity of the PAFs. For the porous network polyimide prepared from triaminotriptycene and 1,4,5,8-naphthalenetetracarboxylic anhydride (STPI-2)[77] a similar conclusion can be reached but in this case justified by experimental data as the equivalent non-network polyimide (TPI7)[78] is not porous. In contrast, the analogous non-network polymer to the highly microporous triptycene-based network polymer (SA_{BET} = 1750 m^2 g^{-1})[79, 80] is PIM-Trip (Fig. 4), which is porous (SA_{BET} = 950 m^2 g^{-1}), therefore, it is possible that IM contributes significantly to the microporosity of this network polymer. It has to be conceded that this analysis is subjective but it may allow the identification of the key PIM structural criteria in a network polymer and, therefore, its classification as a "network-PIM". However, this must be made with the understanding that a highly cross-linked network polymer *does not* require the structural features associated with a PIM to be microporous.

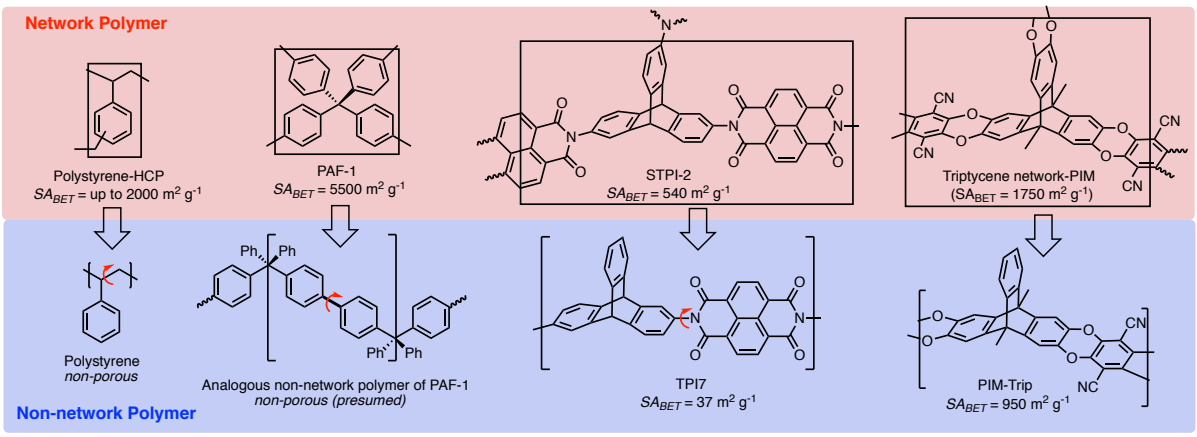

Fig. 4. Analysis of porous network polymers by comparison with analogous non-network polymers as a potential method to determine whether they can be classified as "network-PIMs". Arrows indicate bonds about which there is freedom of rotation.

3. Characteristic properties of PIMs.

3.1. Solubility and solution characterization. Generally, early versions of ladder-polymers were associated with very poor solubility, presumably because most early examples were rigid rod-shaped macromolecules for which efficient packing, via chain alignment, provides strong inter-chain cohesion.[81] More recently, ladder polymer developed for use as optoelectronic materials use long alkyl chains as solubilizing groups.[82] In contrast, PIMs tend to be freely soluble in organic solvents at ambient temperatures without the need for solubilizing groups. This is a key property of PIMs which has enabled their fabrication via solution processing into self-standing films for gas permeability measurements (Section 3.3), composite[83] and hollow fibre membranes,[84] thin films for sensor use[85] and 3D printed objects.[86] Importantly, solubility facilitates commercial roll-to-roll fabrication (e.g. 3M's end of life indicator for their respirator cartridges).[87] The solubility of PIMs implies that their rigid and contorted structure, which ensures inefficient packing in the solid state, also disrupts the extent of cohesive interactions by reducing the area of inter-chain contact. In addition, the IM allows access of solvent into the polymer solid to aid with dissolution. Many PIMs (e.g. PIM-1) are soluble in common low-boiling solvents (e.g. tetrahydrofuran or chloroform) but some (e.g. PIM-BTrip) require the use of high boiling aromatic solvents such as quinoline. It is notable that the rigid fused structure of PIMs means that they possess some

of the highest glass transition temperatures (> 350 °C) for a directly solution-processable organic material.[88]

The solubility of PIMs allows their characterization by solution-based characterisation methods such as NMR and GPC. NMR can be used to confirm the structure of the polymer, however, it is a distinct characteristic of the ^{1}H NMR spectra of PIMs that the peaks are significantly broadened as observed for rod-shaped or helical ladder polymers.[89] This phenomenon is related to greater spin-spin interactions between ^{1}H nuclei in polymers with fixed conformations causing shorter spin-spin relaxation times (T_2). Peak broadening appears correlated to rigidity so that the peaks of PIMs derived from bridged bicyclic structural units (e.g. PIM-EA-TB)[90] appear broader than those derived from spirobisindane (e.g. PIM-1).[91] NMR can also indicate the degree of branching.[91]

Estimation of the molecular mass of PIMs using Gel Permeation Chromatography (GPC) is also facilitated by their solubility. GPC analysis involves measuring the retention time of a polymer sample on a porous column that has been calibrated using standards of well-defined molecular mass, such as polystyrenes prepared via anionic polymerization. For the estimate to be valid, the hydrodynamic radius of the polymer chain has to be similar to that of the random-coil configuration of a polystyrene chain of the same molecular mass. For example, it is known that GPC suggests molecular mass values of rigid-rod polymers that are 50-100% higher than their actual masses.[92] Conversely, the molecular masses of OMIMs and DIMs (Fig. 2), which are highly branched PIM-like structures of known molecular mass (1500-7000 g mol^{-1}), are up to 40% lower than their actual values,[74-76] which is consistent with the smaller values obtained for aromatic dendrimers relative to their non-branched polymer equivalents.[93] Thus, it appears that a contorted chain of a PIM may occupy a similar hydrodynamic radius as the random-coil configuration of a polystyrene chain of the same molecular mass and, therefore, GPC should provide rough estimates of the molecular masses of PIMs.

3.2. Gas adsorption analysis. Among many other physical characterization techniques,[8] nitrogen (N_2) adsorption at 77 K is a standard method for measuring the porosity of solid with the resulting isotherm providing information on pore size and volume.[11] N_2 isotherms from PIMs shown significant adsorption at low relative pressure (P/P_0 < 0.01) indicating the presence of micropores. However, there are key differences between these and the Type I isotherms obtained from conventional microporous materials (e.g. zeolites).[11] Firstly, for

PIMs, there is continued N_2 adsorption at higher relative pressure and, secondly, there is distinct hysteresis between the adsorption and desorption isotherms. These features are consistent with the PIM swelling during N_2 adsorption as a result of the lack of a fixed framework (or flexibility for network-PIMs). Nitrogen isotherms of porous materials are used routinely to calculate the internal surface area using BET theory with the apparent SA_{BET} being routinely reported for PIMs, despite the swelling invalidating the result.[28] Nevertheless, the value of apparent SA_{BET} has some use for making comparisons between different PIMs. Another feature of N_2 adsorption that is often observed for PIMs is the very slow uptake at low partial pressures due to the length of time it takes for the pressure of N_2 in contact with the sample to reach a stable value. This equilibration time is even longer for films than for powdered samples presumably due to the lower external surface area of the films so that some adsorption sites take longer for the N_2 molecules to reach. Nevertheless, it has been possible to obtain isotherms from very thin films and for films of PIMs with greater microporosity. These results imply a slow diffusion of N_2 into the PIM, which is consistent with gas permeability measurements (Section 3.3). The use of smaller gas probes (e.g. H_2 at 77 K or CO_2 at 273 K) allows the investigation of IM without problems associated with slow adsorption or swelling, as demonstrated by the lack of hysteresis between adsorption and desorption isotherms.[28, 29] Such measurements provide evidence that the free volume within the PIMs is easily accessible to these smaller molecules (Section 3.3).

Gas adsorption data can also be used to estimate pore-size distribution (PSD) using, for example, Howarth-Kawazoe analysis, which for PIMs tends to give a smooth PSD from 0.4-1.2 nm with a peak value of ~0.5 nm (Fig. 5a).[94] This is consistent with values obtained from the simulation of chain packing.[95] Often the default PSD analysis on nitrogen adsorption instruments use NonLocal Density Fluctuation Theory (NLDFT) with inappropriate parameter settings for organic microporous materials, resulting in artifacts such as unlikely gaps in the PSD. Parameter settings that give PSDs that are more consistent with those obtained from chain-packing simulations have been proposed by Colina *et al*.[96]

3.3. Gas permeability. The values for gas permeability through a film of a PIM can be used as a direct indicator of the amount of free volume present and, importantly, to assess the potential of the PIM for use as the selective layer in a gas separation membrane. Generally, the gas permeability of a gas x (P_x) through a PIM is very high relative to other types of glassy polymer, with the exception of certain polyacetylenes,[97] such as PTMSP (Fig. 1c),

with values that are several orders of magnitude higher than those of polymers currently used for gas separation membranes.[26, 37, 41, 43, 46, 49-52, 54, 98-106] However, such values for all polymers are not fixed and depend greatly on the history of the film sample prior to measurement. Therefore, it is best to report gas permeabilities from films of different thicknesses, treatments and age to help other researchers understand the true potential of a new polymer. For example, PIM films recently soaked in methanol to remove any remaining casting solvent tend to demonstrate much higher permeability for all gases relative to those that have been left to age (Fig. 5). Such physical aging is a general feature of glassy polymers and involves the loss of free volume over time and is greatly accelerated for thin films.[5] In addition to permeability (P_x), selectivity (P_x/P_y or α_{xy}) for gas *x* over gas *y* is key to the performance of a membrane separation. Generally, polymers suffer from a trade-off between permeability and selectivity that has been quantified by Robeson[107, 108] using double logarithmic plots of P_x versus α_{xy} for each gas pair (*x*/*y*) of interest. In 1991 Robson defined an upper bound for each gas pair based on the data of the best performing polymers.[107] Data for PIMs based on the SBI unit (PIM-1 and PIM-7)[26] contributed to Robeson's 2008 revision of the upper bounds due to their high permeability and moderate selectivity.[108] Subsequently, the use of more rigid structural units such as SBF[41, 43] and particularly bridged bicyclic units such as EA[46, 47] and Trip[49, 50, 102] (Fig. 3) produced PIMs that demonstrate data well above the 2008 upper bound for O_2/N_2, H_2/N_2 and H_2/CH_4 prompting Pinnau to propose the revision of the upper bounds for these gas pairs in 2015.[109] In 2019, revisions for the important CO_2/CH_4 and CO_2/N_2 upper bounds were proposed using data from a series of PIM-BTrip polymers.[52] Generally, the greater selectivity of PIMs relative to other high free volume polymers, such as PTMSP and related polyacetylenes, can be attributed to the distribution of the free volume (i.e. PSD) as determined directly by gas adsorption (Fig. 5a)[94] and by simulations of chain packing (Fig. 5d).[110] For PTMSP, the free volume elements are larger and accessible to both smaller gas molecules such as He and H_2 and larger ones such as N_2 and CH_4. In contrast, the free volume for even the most permeable PIMs is composed of smaller elements that are freely accessible only to smaller gas molecules.[37, 47, 101]

Fuoco *et al*. showed that plotting the diffusivity of a gas (D_x) against the square of its kinetic diameter (d_x^2) gives information on the mechanism of transport through PIMs (Fig. 5c), as diffusion is dependent on gas molecules moving through cylindrical voids of sufficient cross-sectional area.[111] For a typical glassy polymer used for gas separation membranes, diffusivity is low due to the lack of free volume, and the difference between diffusivity for a

smaller gas (e.g. D_{H_2}) may be four orders of magnitude greater that than of a larger gas (e.g. D_{CH_4}). This reflects the activated transport mechanism for which thermal motions of polymer chains are required to open a gap large enough to allow progress of the gas molecule. For ultrapermeable PTMSP, diffusivity is much larger for all gases due to the large size of its free volume elements, so that the difference between D_{H_2} and D_{CH_4} is only one order of magnitude. In addition, rapid rotations about the long Si-C bonds allow the $Si(CH_3)_3$ groups to act as turnstiles allowing larger gas molecules to move easily from one element of free volume to another. Therefore, gas transport is via pore diffusion similar to that observed for conventional porous materials with pores of diameter > 1 nm.

For PIMs, gas diffusivity is high, consistent with intrinsic microporosity providing pathways for rapid transport, but the difference between D_{H_2} and D_{CH_4} is higher than that for PTMSP by an additional order of magnitude. For the larger gases (O_2, N_2, CO_2 and CH_4), the gradient of the correlation between D_x and d_x^2 is similar to that of a conventional glassy polymer indicating excellent size-sieving performance, which is due to the highly rigid PIM chains restricting the opening of large voids between free volume elements. Distinctively for PIMs, the diffusivity data for the smaller gases (H_2 and He) does not lie on the same D_x *versus* d_x^2 correlation as that of the larger gases. This non-linearity is interpreted as the transport of H_2 and He being predominantly via the pore diffusion mechanism, with very low activation energy for diffusivity;[112] whereas, the transport of larger gases is controlled by the activated solution-diffusion mechanism of conventional glassy polymers.[111] Hence, PIMs act like true microporous materials for small gas molecules, which experience the intrinsic microporosity as being fully accessible and interconnected, but behave more like conventional glassy polymers for larger gases (Fig. 5d). Although much less studied than gas permeability, the selective transport of ions though PIMs is of growing importance for the development of electrochemical catalysts[113-115], sensors[116] and batteries.[117-121] Similar size selectivity mechanisms to those elucidated for gases are being found for ions, with the rigidity of the PIM chain enhancing the selective transport of smaller ions over larger ions.[122]

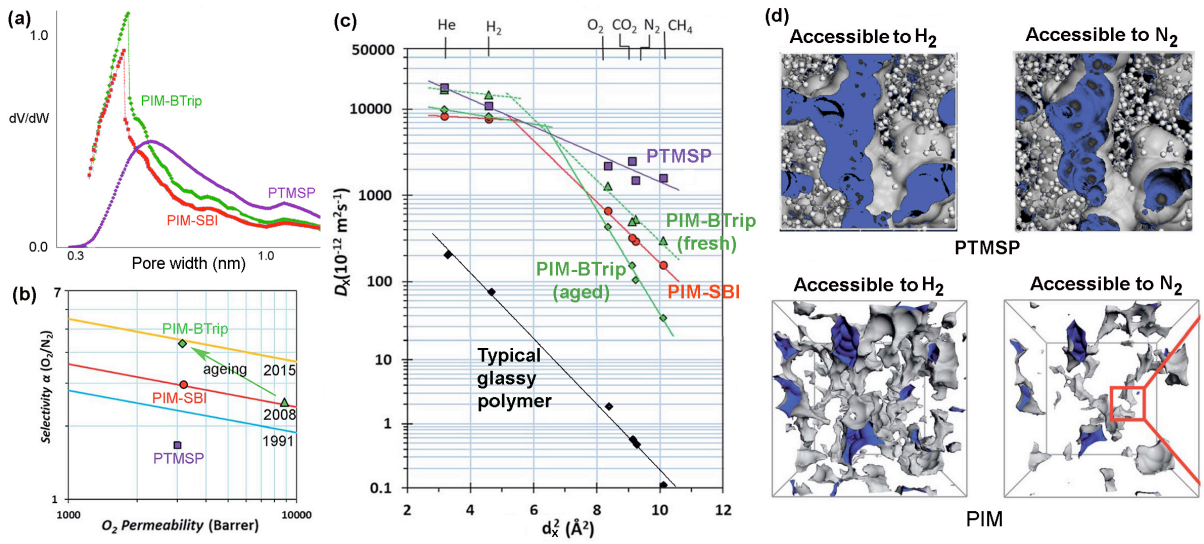

Fig 5. Comparisons of data for a PIM based on SBI, a PIM based on BTrip (fresh and aged film) and PTMSP: (a) Pore size distributions (b) O_2/N_2 Robeson plot and (c) plot of gas diffusivity (D_x) *versus* the square of the gas effective diameter (d_x^2). (d) Representations of the free volume (shaded purple) that is accessible to H_2 (left) and N_2 (right) both for PTMSP[110] (top) and a PIM[101] (bottom).

4. Conclusions

To conclude, the distinct macromolecular structure of PIMs provides organic materials with a unique combination of properties including good solubility, exceptional chain rigidity, and high free volume, which support the rapid and selective transport of small molecules. PIMs are directly solution-processable into useful forms such as membranes that can act as efficient molecular sieves. A revised definition of a PIM is proposed as a "*Polymer that is composed of a fully (or predominantly) fused-ring macromolecular chain that is fixed in a 2D or 3D random coil conformation due to sites of contortion, such as bridged bicyclic or spirocyclic units, so that they pack space inefficiently in the solid state*". Beyond this definition there are (and are likely to be developed) polymers that demonstrate some PIM-like characteristics and so a more detailed summary of the distinctive features of PIM synthesis, structure and properties is given below.

Synthesis:

- Aromatic monomers are reacted in step-growth polymerizations based on reactions that involve forming more than one covalent bond for each monomer incorporated into the polymer chain.

Structural:

- Polymer chains are composed of aromatic rings fused together by spirocyclic, bridged bicyclic or other fused ring units so that they are fixed in a 2D or 3D random coil.
- If single bonds are present (e.g. imide C-N) sufficient steric crowding must prohibit the rotation of one aromatic ring relative to its neighbour to maintain the fixed conformation of the random coil and to ensure frustrated chain packing.
- Network polymers with these structural features may be considered as PIMs, however, not all of their porosity is likely to arise from intrinsic microporosity.

Properties:

- Non-network structures are typically soluble in organic solvents, from which they will form amorphous powders by precipitation or glassy films by slow evaporation (if their molecular mass is sufficiently high).
- Polymer rigidity and fixed chain conformation results in broadened peaks in ^{1}H NMR spectra and very high glass transition temperatures.
- Solids possess large amounts of free volume which is freely accessible to smaller gas molecules via pore diffusion and may be accessible to larger molecules via an activated diffusion process often accompanied by swelling.
- The rigidity of the polymer chains provides good size-selectivity for gases and ions due to the high activation energy required to open a void of sufficient size to allow larger molecules to move between elements of free volume.

Acknowledgements.

I am grateful to the many researchers who have contributed to the diversity, understanding and applications of PIMs.

References

[1] N.B. McKeown, P.M. Budd, B. Ghanem, K. Msayib, Microporous polymer material, International patent PCT WO 2005/012397 (2005).

[2] P.M. Budd, B.S. Ghanem, S. Makhseed, N.B. McKeown, K.J. Msayib, C.E. Tattershall, Polymers of intrinsic microporosity (PIMs): robust, solution-processable, organic nanoporous materials, Chem. Commun. (2004) 230-231. https://doi.org/10.1039/b311764b
[3] N.B. McKeown, P.M. Budd, Polymers of intrinsic microporosity (PIMs): organic materials for membrane separations, heterogeneous catalysis and hydrogen storage, Chem. Soc. Rev. 35 (2006) 675-683. https://doi.org/10.1039/b600349d
[4] N.B. McKeown, The synthesis of polymers of intrinsic microporosity (PIMs), Sci China Chem 60 (2017) 1023-1032. https://doi.org/10.1007/s11426-017-9058-x
[5] Z.X. Low, P.M. Budd, N.B. McKeown, D.A. Patterson, Gas Permeation Properties, Physical Aging, and Its Mitigation in High Free Volume Glassy Polymers, Chem. Rev. 118 (2018) 5871-5911. https://doi.org/10.1021/acs.chemrev.7b00629
[6] M. Usman, A. Ahmed, B. Yu, Q. Peng, Y. Shen, H. Cong, A review of different synthetic approaches of amorphous intrinsic microporous polymers and their potential applications in membrane-based gases separation, Eur. Polym. J. 120 (2019) 109262. https://doi.org/10.1016/j.eurpolymj.2019.109262
[7] Y. Wang, X. Ma, B.S. Ghanem, F. Alghunaimi, I. Pinnau, Y. Han, Polymers of intrinsic microporosity for energy-intensive membrane-based gas separations, Materials Today Nano 3 (2018) 69-95. https://doi.org/10.1016/j.mtnano.2018.11.003
[8] P.M. Budd, in *Sustainable Nanoscale Engineering*, eds. G. Szekely and A. Livingston, Elsevier, 2020, DOI: 10.1016/B978-0-12-814681-1.00009-6, pp. 231-264.
[9] H. Zhou, W. Jin, Membranes with Intrinsic Micro-Porosity: Structure, Solubility, and Applications, Membranes 9 (2019) 3. https://doi.org/10.3390/membranes9010003
[10] S. Kim, Y.M. Lee, Rigid and microporous polymers for gas separation membranes, Prog. Polym. Sci. 43 (2015) 1-32. https://doi.org/10.1016/j.progpolymsci.2014.10.005
[11] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure Appl. Chem. 87 (2015) 1051-1069. https://doi.org/10.1515/pac-2014-1117
[12] M.S. Silverstein, The Chemistry of Porous Polymers: The Holey Grail, Isr. J. Chem. 60 (2020) 140-150. https://doi.org/10.1002/ijch.202000003
[13] M.P. Tsyurupa, V.A. Davankov, Porous structure of hypercrosslinked polystyrene: State-of-the-art mini-review, Reactive & Functional Polymers 66 (2006) 768-779. https://doi.org/10.1016/j.reactfunctpolym.2005.11.004
[14] T. Ben, H. Ren, S.Q. Ma, D.P. Cao, J.H. Lan, X.F. Jing, W.C. Wang, J. Xu, F. Deng, J.M. Simmons, S.L. Qiu, G.S. Zhu, Targeted Synthesis of a Porous Aromatic Framework with High Stability and Exceptionally High Surface Area, Angew Chem Int Edit 48 (2009) 9457-9460. https://doi.org/10.1002/anie.200904637
[15] R. Dawson, A.I. Cooper, D.J. Adams, Nanoporous organic polymer networks, Prog. Polym. Sci. 37 (2012) 530-563. https://doi.org/10.1016/j.progpolymsci.2011.09.002
[16] H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, The Chemistry and Applications of Metal-Organic Frameworks, Science 341 (2013) 974. https://doi.org/10.1126/science.1230444
[17] C.S. Diercks, O.M. Yaghi, The atom, the molecule, and the covalent organic framework, Science 355 (2017) eaal1585. https://doi.org/10.1126/science.aal1585
[18] N.B. McKeown, H. Li, S. Makhseed, Towards phthalocyanine network polymers for heterogeneous catalysis, Supported Catalysts and their Applications (2001) 214-217.
[19] N.B. McKeown, S. Hanif, K. Msayib, C.E. Tattershall, P.M. Budd, Porphyrin-based nanoporous network polymers, Chem. Commun. (2002) 2782-2783. https://doi.org/10.1039/B208702M
[20] N.B. McKeown, S. Makhseed, P.M. Budd, Phthalocyanine-based nanoporous network polymers, Chem. Commun., (2002) 2780-2781. https://doi.org/10.1039/B207642J
[21] H.J. Mackintosh, P.M. Budd, N.B. McKeown, Catalysis by microporous phthalocyanine and porphyrin network polymers, J. Mater. Chem. 18 (2008) 573-578. https://doi.org/10.1039/b715660j

[22] P.M. Budd, E.S. Elabas, B.S. Ghanem, S. Makhseed, N.B. McKeown, K.J. Msayib, C.E. Tattershall, D. Wang, Solution-processed, organophilic membrane derived from a polymer of intrinsic microporosity, Adv. Mater. 16 (2004) 456-460. https://doi.org/10.1002/adma.200306053
[23] T. Masuda, E. Isobe, T. Higashimura, K. Takada, Poly 1-(trimethylsilyl)-1-propyne - a new high polymer synthesized with transition-metal catalysts and characterized by extremely high gas-permeability, J. Am. Chem. Soc. 105 (1983) 7473-7474. https://doi.org/10.1021/ja00363a061
[24] R. Srinivasan, S.R. Auvil, P.M. Burban, Elucidating the mechanism(s) of gas-transport in poly 1-(trimethylsilyl)-1-propyne (PTMSP) membranes, J. Membr. Sci. 86 (1994) 67-86. https://doi.org/10.1016/0376-7388(93)e0128-7
[25] L. Starannikova, V. Khodzhaeva, Y. Yampolskii, Mechanism of aging of poly 1-(trimethylsilyl)-1 propyne and its effect on gas permeability, J. Membr. Sci. 244 (2004) 183-191. https://doi.org/10.1016/j.memsci.2004.06.051
[26] P.M. Budd, K.J. Msayib, C.E. Tattershall, B.S. Ghanem, K.J. Reynolds, N.B. McKeown, D. Fritsch, Gas separation membranes from polymers of intrinsic microporosity, J. Membr. Sci. 251 (2005) 263-269. https://doi.org/10.1016/j.memsci.2005.01.009
[27] R.R. Tiwari, Z.P. Smith, H.Q. Lin, B.D. Freeman, D.R. Paul, Gas permeation in thin films of "high free-volume" glassy perfluoropolymers: Part I. Physical aging, Polymer 55 (2014) 5788-5800. https://doi.org/10.1016/j.polymer.2014.09.022
[28] M. Minelli, D.R. Paul, G.C. Sarti, On the interpretation of cryogenic sorption isotherms in glassy polymers, J. Membr. Sci. 540 (2017) 229-242. https://doi.org/10.1016/j.memsci.2017.06.053
[29] M. Minelli, B.R. Pimentel, M.L. Jue, R.P. Lively, G.C. Sarti, Analysis and utilization of cryogenic sorption isotherms for high free volume glassy polymers, Polymer 170 (2019) 157-167. https://doi.org/10.1016/j.polymer.2019.03.012
[30] K.E. Hart, L.J. Abbott, C.M. Colina, Analysis of force fields and BET theory for polymers of intrinsic microporosity, Molecular Simulation 39 (2013) 397-404. https://doi.org/10.1080/08927022.2012.733945
[31] T.M. Long, T.M. Swager, Minimization of free volume: Alignment of triptycenes in liquid crystals and stretched polymers, Adv. Mater. 13 (2001) 601-+. https://doi.org/10.1002/1521-4095(200104)13:8<601::Aid-adma601>3.0.Co;2-v
[32] Y. Jiao, F.H. Stillinger, S. Torquato, Optimal packings of superballs, Physical Review E 79 (2009). https://doi.org/10.1103/PhysRevE.79.041309
[33] N.T. Tsui, A.J. Paraskos, L. Torun, T.M. Swager, E.L. Thomas, Minimization of internal molecular free volume: A mechanism for the simultaneous enhancement of polymer stiffness, strength, and ductility, Macromolecules 39 (2006) 3350-3358. https://doi.org/10.1021/ma060047q
[34] T.M. Long, T.M. Swager, Molecular design of free volume as a route to low-kappa dielectric materials, J. Am. Chem. Soc. 125 (2003) 14113-14119. https://doi.org/10.1021/ja0360945
[35] M. Heuchel, D. Fritsch, P.M. Budd, N.B. McKeown, D. Hofmann, Atomistic packing model and free volume distribution of a polymer with intrinsic microporosity (PIM-1), J. Membr. Sci. 318 (2008) 84-99. https://doi.org/10.1016/j.memsci.2008.02.038
[36] K.E. Hart, J.M. Springmeier, N.B. McKeown, C.M. Colina, Simulated swelling during low-temperature N-2 adsorption in polymers of intrinsic microporosity, PCCP 15 (2013) 20161-20169. https://doi.org/10.1039/c3cp53402b
[37] I. Rose, C.G. Bezzu, M. Carta, B. Comesana-Gandara, E. Lasseuguette, M.C. Ferrari, P. Bernardo, G. Clarizia, A. Fuoco, J.C. Jansen, K.E. Hart, T.P. Liyana-Arachchi, C.M. Colina, N.B. McKeown, Polymer ultrapermeability from the inefficient packing of 2D chains, Nat Mater 16 (2017) 932-937. https://doi.org/10.1038/Nmat4939
[38] G.S. Larsen, K.E. Hart, C.M. Colina, Predictive simulations of the structural and adsorptive properties for PIM-1 variations, Molecular Simulation 40 (2014) 599-609. https://doi.org/10.1080/08927022.2013.829222

[39] N.B. McKeown, P.M. Budd, Exploitation of Intrinsic Microporosity in Polymer-Based Materials, Macromolecules 43 (2010) 5163-5176. https://doi.org/10.1021/ma1006396
[40] N.B. McKeown, P.M. Budd, in *Encyclopedia of Polymer Science and Technology*, 2009, DOI: 10.1002/0471440264.pst563.
[41] C.G. Bezzu, M. Carta, A. Tonkins, J.C. Jansen, P. Bernardo, F. Bazzarelli, N.B. McKeown, A Spirobifluorene-Based Polymer of Intrinsic Microporosity with Improved Performance for Gas Separation, Adv. Mater. 24 (2012) 5930-5935. https://doi.org/10.1002/adma.201202393
[42] X. Ma, O. Salinas, E. Litwiller, I. Pinnau, Novel Spirobifluorene- and Dibromospirobifluorene-Based Polyimides of Intrinsic Microporosity for Gas Separation Applications, Macromolecules 46 (2013) 9618-9624.
[43] C.G. Bezzu, M. Carta, M.C. Ferrari, J.C. Jansen, M. Monteleone, E. Esposito, A. Fuoco, K. Hart, T.P. Liyana-Arachchi, C.M. Colina, N.B. McKeown, The synthesis, chain-packing simulation and long-term gas permeability of highly selective spirobifluorene-based polymers of intrinsic microporosity, J Mater Chem A 6 (2018) 10507-10514. https://doi.org/10.1039/c8ta02601g
[44] T. Emmler, K. Heinrich, D. Fritsch, P.M. Budd, N. Chaukura, D. Ehlers, K. Ratzke, F. Faupel, Free Volume Investigation of Polymers of Intrinsic Microporosity (PIMs): PIM-1 and PIM1 Copolymers Incorporating Ethanoanthracene Units, Macromolecules 43 (2010) 6075-6084. https://doi.org/10.1021/ma1008786
[45] E. Tocci, L. De Lorenzo, P. Bernardo, G. Clarizia, F. Bazzarelli, N.B. McKeown, M. Carta, R. Malpass-Evans, K. Friess, K. Pilnacek, M. Lanc, Y.P. Yampolskii, L. Strarannikova, V. Shantarovich, M. Mauri, J.C. Jansen, Molecular Modeling and Gas Permeation Properties of a Polymer of Intrinsic Microporosity Composed of Ethanoanthracene and Troger's Base Units, Macromolecules 47 (2014) 7900-7916. https://doi.org/10.1021/ma501469m
[46] M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, J.C. Jansen, P. Bernardo, F. Bazzarelli, N.B. McKeown, An Efficient Polymer Molecular Sieve for Membrane Gas Separations, Science 339 (2013) 303-307. https://doi.org/10.1126/science.1228032
[47] Y. Rogan, R. Malpass-Evans, M. Carta, M. Lee, J.C. Jansen, P. Bernardo, G. Clarizia, E. Tocci, K. Friess, M. Lanc, N.B. McKeown, A highly permeable polyimide with enhanced selectivity for membrane gas separations, J Mater Chem A 2 (2014) 4874-4877. https://doi.org/10.1039/c4ta00564c
[48] B.S. Ghanem, A facile synthesis of a novel triptycene-containing A-B monomer: precursor to polymers of intrinsic microporosity, Polymer Chemistry 3 (2012) 96-98. https://doi.org/10.1039/c1py00423a
[49] M. Carta, M. Croad, R. Malpass-Evans, J.C. Jansen, P. Bernardo, G. Clarizia, K. Friess, M. Lanc, N.B. McKeown, Triptycene Induced Enhancement of Membrane Gas Selectivity for Microporous Troger's Base Polymers, Adv. Mater. 26 (2014) 3526-3531. https://doi.org/10.1002/adma.201305783
[50] B.S. Ghanem, R. Swaidan, E. Litwiller, I. Pinnau, Ultra-Microporous Triptycene-based Polyimide Membranes for High-Performance Gas Separation, Adv. Mater. 26 (2014) 3688-3692. https://doi.org/10.1002/adma.201306229
[51] I. Rose, M. Carta, R. Malpass-Evans, M.-C. Ferrari, P. Bernardo, G. Clarizia, J.C. Jansen, N.B. McKeown, Highly Permeable Benzotriptycene-Based Polymer of Intrinsic Microporosity, Acs Macro Lett 4 (2015) 912-915. https://doi.org/10.1021/acsmacrolett.5b00439
[52] B. Comesaña-Gándara, J. Chen, C.G. Bezzu, M. Carta, I. Rose, M.-C. Ferrari, E. Esposito, A. Fuoco, J.C. Jansen, N.B. McKeown, Redefining the Robeson upper bounds for CO_2/CH_4 and CO_2/N_2 separations using a series of ultrapermeable benzotriptycene-based polymers of intrinsic microporosity, Energy & Environmental Science 12 (2019) 2733-2740. https://doi.org/10.1039/C9EE01384A
[53] M. Carta, R. Malpass-Evans, M. Croad, Y. Rogan, M. Lee, I. Rose, N.B. McKeown, The synthesis of microporous polymers using Troger's base formation, Polymer Chemistry 5 (2014) 5267-5272. https://doi.org/10.1039/c4py00609g

[54] M. Lee, C.G. Bezzu, M. Carta, P. Bernardo, G. Clarizia, J.C. Jansen, N.B. McKeown, Enhancing the Gas Permeability of Troger's Base Derived Polyimides of Intrinsic Microporosity, Macromolecules 49 (2016) 4147-4154. https://doi.org/10.1021/acs.macromol.6b00351
[55] B.S. Ghanem, N.B. McKeown, P.M. Budd, J.D. Selbie, D. Fritsch, High-performance membranes from polyimides with intrinsic microporosity, Adv. Mater. 20 (2008) 2766-2771. https://doi.org/10.1002/adma.200702400
[56] B.S. Ghanem, N.B. McKeown, P.M. Budd, N.M. Al-Harbi, D. Fritsch, K. Heinrich, L. Starannikova, A. Tokarev, Y. Yampolskii, Synthesis, Characterization, and Gas Permeation Properties of a Novel Group of Polymers with Intrinsic Microporosity: PIM-Polyimides, Macromolecules 42 (2009) 7881-7888. https://doi.org/10.1021/ma901430q
[57] Y. Rogan, L. Starannikova, V. Ryzhikh, Y. Yampolskii, P. Bernardo, F. Bazzarelli, J.C. Jansen, N.B. McKeown, Synthesis and gas permeation properties of novel spirobisindane-based polyimides of intrinsic microporosity, Polymer Chemistry 4 (2013) 3813-3820. https://doi.org/10.1039/c3py00451a
[58] H.W.H. Lai, S. Liu, Y. Xia, Norbornyl Benzocyclobutene Ladder Polymers: Conformation and Microporosity, J Polym Sci Pol Chem 55 (2017) 3075-3081. https://doi.org/10.1002/pola.28640
[59] H.W.H. Lai, Y.C. Teo, Y. Xia, Functionalized Rigid Ladder Polymers from Catalytic Arene-Norbornene Annulation Polymerization, Acs Macro Lett 6 (2017) 1357-1361. https://doi.org/10.1021/acsmacrolett.7b00806
[60] H.W.H. Lai, F.M. Benedetti, Z. Jin, Y.C. Teo, A.X. Wu, M.G.D. Angelis, Z.P. Smith, Y. Xia, Tuning the Molecular Weights, Chain Packing, and Gas-Transport Properties of CANAL Ladder Polymers by Short Alkyl Substitutions, Macromolecules 52 (2019) 6294-6302. https://doi.org/10.1021/acs.macromol.9b01155
[61] B.L. Schurmann, V. Enkelmann, M. Loffler, A.D. Schluter, On The Shape Of A Diels-Alder Ladder Polymer, Angewandte Chemie-International Edition in English 32 (1993) 123-125. https://doi.org/10.1002/anie.199301231
[62] S.W. Thomas, T.M. Long, B.D. Pate, S.R. Kline, E.L. Thomas, T.M. Swager, Perpendicular organization of macromolecules: Synthesis and alignment studies of a soluble poly(iptycene), J. Am. Chem. Soc. 127 (2005) 17976-17977. https://doi.org/10.1021/ja056241u
[63] N. Du, G.P. Robertson, J. Song, I. Pinnau, M.D. Guiver, High-Performance Carboxylated Polymers of Intrinsic Microporosity (PIMs) with Tunable Gas Transport Properties, Macromolecules 42 (2009) 6038-6043. https://doi.org/10.1021/ma9009017
[64] B. Santoso, P. Yanaranop, H. Kang, I.K.H. Leung, J. Jin, A Critical Update on the Synthesis of Carboxylated Polymers of Intrinsic Microporosity (C-PIMs), Macromolecules 50 (2017) 3043-3050. https://doi.org/10.1021/acs.macromol.7b00344
[65] B. Satilmis, M. Lanc, A. Fuoco, C. Rizzuto, E. Tocci, P. Bernardo, G. Clarizia, E. Esposito, M. Monteleone, M. Dendisova, K. Friess, P.M. Budd, J.C. Jansen, Temperature and pressure dependence of gas permeation in amine-modified PIM-1, J. Membr. Sci. 555 (2018) 483-496. https://doi.org/10.1016/j.memsci.2018.03.039
[66] C.R. Mason, L. Maynard-Atem, N.M. Al-Harbi, P.M. Budd, P. Bernardo, F. Bazzarelli, G. Clarizia, J.C. Jansen, Polymer of Intrinsic Microporosity Incorporating Thioamide Functionality: Preparation and Gas Transport Properties, Macromolecules 44 (2011) 6471-6479. https://doi.org/10.1021/ma200918h
[67] N. Du, G.P. Robertson, M.M. Dal-Cin, L. Scoles, M.D. Guiver, Polymers of intrinsic microporosity (PIMs) substituted with methyl tetrazole, Polymer 53 (2012) 4367-4372. https://doi.org/10.1016/j.polymer.2012.07.055
[68] N. Du, H.B. Park, G.P. Robertson, M.M. Dal-Cin, T. Visser, L. Scoles, M.D. Guiver, Polymer nanosieve membranes for CO2-capture applications, Nat Mater 10 (2011) 372-375. https://doi.org/10.1038/nmat2989
[69] H.A. Patel, C.T. Yavuz, Noninvasive functionalization of polymers of intrinsic microporosity for enhanced CO2 capture, Chem. Commun. 48 (2012) 9989-9991. https://doi.org/10.1039/c2cc35392j

[70] Z. Yang, R. Guo, R. Malpass-Evans, M. Carta, N.B. McKeown, M.D. Guiver, L. Wu, T. Xu, Highly Conductive Anion-Exchange Membranes from Microporous Troger□s Base Polymers, Angew Chem Int Edit 55 (2016) 11499–11502 https://doi.org/DOI: 10.1002/anie.201605916
[71] N.B. McKeown, Organic Molecules of Intrinsic Microporosity, Organic Materials 02 (2020) 020-025. https://doi.org/10.1055/s-0039-3402512
[72] B. Kohl, F. Rominger, M. Mastalerz, Crystal Structures of a Molecule Designed Not To Pack Tightly, Chem. Eur. J. 21 (2015) 17308-17313. https://doi.org/10.1002/chem.201502847
[73] L.J. Abbott, A.G. McDermott, A. Del Regno, R.G.D. Taylor, C.G. Bezzu, K.J. Msayib, N.B. McKeown, F.R. Siperstein, J. Runt, C.M. Colina, Characterizing the Structure of Organic Molecules of Intrinsic Microporosity by Molecular Simulations and X-ray Scattering, J. Phys. Chem. B 117 (2013) 355-364. https://doi.org/10.1021/jp308798u
[74] R.G.D. Taylor, M. Carta, C.G. Bezzu, J. Walker, K.J. Msayib, B.M. Kariuki, N.B. McKeown, Triptycene-Based Organic Molecules of Intrinsic Microporosity, Org. Lett. 16 (2014) 1848-1851. https://doi.org/10.1021/ol500591q
[75] R.G.D. Taylor, C.G. Bezzu, M. Carta, K.J. Msayib, J. Walker, R. Short, B.M. Kariuki, N.B. McKeown, The Synthesis of Organic Molecules of Intrinsic Microporosity Designed to Frustrate Efficient Molecular Packing, Chem-Eur J 22 (2016) 2466-2472. https://doi.org/10.1002/chem.201504212
[76] R.G.D. Taylor, Organic Molecules, Dendrimers and Sulfur- based Polymers of Intrinsic Microporosity, PhD thesis, Cardiff University (2013).
[77] C. Zhang, T.L. Zhai, J.J. Wang, Z. Wang, J.M. Liu, B. Tan, X.L. Yang, H.B. Xu, Triptycene-based microporous polyimides: Synthesis and their high selectivity for CO2 capture, Polymer 55 (2014) 3642-3647. https://doi.org/10.1016/j.polymer.2014.06.074
[78] S.A. Sydlik, Z.H. Chen, T.M. Swager, Triptycene Polyimides: Soluble Polymers with High Thermal Stability and Low Refractive Indices, Macromolecules 44 (2011) 976-980. https://doi.org/10.1021/ma101333p
[79] B.S. Ghanem, K.J. Msayib, N.B. McKeown, K.D.M. Harris, Z. Pan, P.M. Budd, A. Butler, J. Selbie, D. Book, A. Walton, A triptycene-based polymer of intrinsic microposity that displays enhanced surface area and hydrogen adsorption, Chem. Commun., DOI: 10.1039/b614214a (2007) 67-69. https://doi.org/10.1039/b614214a
[80] B.S. Ghanem, M. Hashem, K.D.M. Harris, K.J. Msayib, M. Xu, P.M. Budd, N. Chaukura, D. Book, S. Tedds, A. Walton, N.B. McKeown, Triptycene-Based Polymers of Intrinsic Microporosity: Organic Materials That Can Be Tailored for Gas Adsorption, Macromolecules 43 (2010) 5287-5294. https://doi.org/10.1021/ma100640m
[81] R. Wolf, C.S. Marvel, Polymers With Quinoxaline Units .V. Polymers With Quinoxaline And Dioxin Units, Journal of Polymer Science Part a-1-Polymer Chemistry 7 (1969) 2481-&. https://doi.org/10.1002/pol.1969.150070902
[82] U. Scherf, Ladder-type materials, J. Mater. Chem. 9 (1999) 1853-1864. https://doi.org/10.1039/a900447e
[83] D. Fritsch, P. Merten, K. Heinrich, M. Lazar, M. Priske, High performance organic solvent nanofiltration membranes: Development and thorough testing of thin film composite membranes made of polymers of intrinsic microporosity (PIMs), J. Membr. Sci. 401 (2012) 222-231. https://doi.org/10.1016/j.memsci.2012.02.008
[84] M.L. Jue, V. Breedveld, R.P. Lively, Defect-free PIM-1 hollow fiber membranes, J. Membr. Sci. 530 (2017) 33-41. https://doi.org/10.1016/j.memsci.2017.02.012
[85] N.A. Rakow, M.S. Wendland, J.E. Trend, R.J. Poirier, D.M. Paolucci, S.P. Maki, C.S. Lyons, M.J. Swierczek, Visual Indicator for Trace Organic Volatiles, Langmuir 26 (2010) 3767-3770. https://doi.org/10.1021/la903483q
[86] F.Y. Zhang, Y. Ma, J.S. Liao, V. Breedveld, R.P. Lively, Solution-Based 3D Printing of Polymers of Intrinsic Microporosity, Macromol. Rapid Commun. 39 (2018). https://doi.org/10.1002/marc.201800274

[87] Y. Wang, N.B. McKeown, K.J. Msayib, G.A. Turnbull, I.D.W. Samuel, Laser Chemosensor with Rapid Responsivity and Inherent Memory Based on a Polymer of Intrinsic Microporosity, Sensors 11 (2011) 2478-2487. https://doi.org/10.3390/s110302478
[88] H. Yin, B. Yang, Y.Z. Chua, P. Szymoniak, M. Carta, R. Malpass-Evans, N.B. McKeown, W.J. Harrison, P.M. Budd, C. Schick, M. Böhning, A. Schönhals, Effect of Backbone Rigidity on the Glass Transition of Polymers of Intrinsic Microporosity Probed by Fast Scanning Calorimetry, Acs Macro Lett 8 (2019) 1022-1028. https://doi.org/10.1021/acsmacrolett.9b00482
[89] T. Ikai, T. Yoshida, K. Shinohara, T. Taniguchi, Y. Wada, T.M. Swager, Triptycene-Based Ladder Polymers with One-Handed Helical Geometry, J. Am. Chem. Soc. 141 (2019) 4696-4703. https://doi.org/10.1021/jacs.8b13865
[90] F. Ishiwari, N. Takeuchi, T. Sato, H. Yamazaki, R. Osuga, J.N. Kondo, T. Fukushima, Rigid-to-Flexible Conformational Transformation: An Efficient Route to Ring-Opening of a Troger's Base-Containing Ladder Polymer, Acs Macro Lett 6 (2017) 775-780. https://doi.org/10.1021/acsmacrolett.7b00385
[91] A.B. Foster, M. Tamaddondar, J.M. Luque-Alled, W.J. Harrison, Z. Li, P. Gorgojo, P.M. Budd, Understanding the Topology of the Polymer of Intrinsic Microporosity PIM-1: Cyclics, Tadpoles, and Network Structures and Their Impact on Membrane Performance, Macromolecules 53 (2020) 569-583. https://doi.org/10.1021/acs.macromol.9b02185
[92] H.L. Ricks, U.H. Choudry, A.R. Marshall, U.H.F. Bunz, Rod vs coil: Molecular weight comparison of a poly(dialkyl-p-phenyleneethynylene) with its reduced poly(2,5-dialkyl-p-xylylene), Macromolecules 36 (2003) 1424-1425. https://doi.org/10.1021/ma025630v
[93] C.J. Hawker, E.E. Malmstrom, C.W. Frank, J.P. Kampf, Exact linear analogs of dendritic polyether macromolecules: Design, synthesis, and unique properties, J. Am. Chem. Soc. 119 (1997) 9903-9904. https://doi.org/10.1021/ja972027x
[94] P.M. Budd, N.B. McKeown, D. Fritsch, Free volume and intrinsic microporosity in polymers, J. Mater. Chem. 15 (2005) 1977-1986. https://doi.org/10.1039/b417402j
[95] G.S. Larsen, P. Lin, K.E. Hart, C.M. Colina, Molecular Simulations of PIM-1-like Polymers of Intrinsic Microporosity, Macromolecules 44 (2011) 6944-6951. https://doi.org/10.1021/ma200345v
[96] G. Kupgan, T.P. Liyana-Arachchi, C.M. Colina, NLDFT Pore Size Distribution in Amorphous Microporous Materials, Langmuir 33 (2017) 11138-11145. https://doi.org/10.1021/acs.langmuir.7b01961
[97] Y. Yampolskii, A Current Position of Polyacetylenes Among Other Highly Permeable Membrane Materials, Polymer Reviews 57 (2017) 200-212. https://doi.org/10.1080/15583724.2015.1127960
[98] P.M. Budd, N.B. McKeown, B.S. Ghanem, K.J. Msayib, D. Fritsch, L. Starannikova, N. Belov, O. Sanfirova, Y. Yampolskii, V. Shantarovich, Gas permeation parameters and other physicochemical properties of a polymer of intrinsic microporosity: Polybenzodioxane PIM-1, J. Membr. Sci. 325 (2008) 851-860. https://doi.org/10.1016/j.memsci.2008.09.010
[99] B.S. Ghanem, N.B. McKeown, P.M. Budd, D. Fritsch, Polymers of intrinsic microporosity derived from bis(phenazyl) monomers, Macromolecules 41 (2008) 1640-1646. https://doi.org/10.1021/ma071846r
[100] R. Swaidan, M. Al-Saeedi, B. Ghanem, E. Litwiller, I. Pinnau, Rational Design of Intrinsically Ultramicroporous Polyimides Containing Bridgehead-Substituted Triptycene for Highly Selective and Permeable Gas Separation Membranes, Macromolecules 47 (2014) 5104-5114. https://doi.org/10.1021/ma5009226
[101] R. Williams, L.A. Burt, E. Esposito, J.C. Jansen, E. Tocci, C. Rizzuto, M. Lanc, M. Carta, N.B. McKeown, A highly rigid and gas selective methanopentacene-based polymer of intrinsic microporosity derived from Troger's base polymerization, J Mater Chem A 6 (2018) 5661-5667. https://doi.org/10.1039/c8ta00509e
[102] B.S. Ghanem, R. Swaidan, X. Ma, E. Litwiller, I. Pinnau, Energy-Efficient Hydrogen Separation by AB-Type Ladder-Polymer Molecular Sieves, Adv. Mater. 26 (2014) 6696-6700. https://doi.org/10.1002/adma.201401328

[103] B. Ghanem, F. Alghunaimi, X. Ma, N. Alaslai, I. Pinnau, Synthesis and characterization of novel triptycene dianhydrides and polyimides of intrinsic microporosity based on 3, 3′-dimethylnaphthidine, Polymer 101 (2016) 225-232. https://doi.org/10.1016/j.polymer.2016.08.075
[104] B.S. Ghanem, F. Alghunaimi, Y.G. Wang, G. Genduso, I. Pinnau, Synthesis of Highly Gas-Permeable Polyimides of Intrinsic Microporosity Derived from 1,3,6,8-Tetramethyl-2,7-diaminotriptycene, Acs Omega 3 (2018) 11874-11882. https://doi.org/10.1021/acsomega.8b01975
[105] M.A. Abdulhamid, H.W.H. Lai, Y. Wang, Z. Jin, Y.C. Teo, X. Ma, I. Pinnau, Y. Xia, Microporous Polyimides from Ladder Diamines Synthesized by Facile Catalytic Arene–Norbornene Annulation as High-Performance Membranes for Gas Separation, Chem. Mater. 31 (2019) 1767-1774. https://doi.org/10.1021/acs.chemmater.8b05359
[106] S. Yi, B. Ghanem, Y. Liu, I. Pinnau, W.J. Koros, Ultraselective glassy polymer membranes with unprecedented performance for energy-efficient sour gas separation, Science Advances 5 (2019) eaaw5459. https://doi.org/10.1126/sciadv.aaw5459
[107] L.M. Robeson, Robeson plot (DB), J. Membr. Sci. 62 (1991) 165-186.
[108] L.M. Robeson, The upper bound revisited, J. Membr. Sci. 320 (2008) 390-400. https://doi.org/10.1016/j.memsci.2008.04.030
[109] R. Swaidan, B. Ghanem, I. Pinnau, Fine-Tuned Intrinsically Ultramicroporous Polymers Redefine the Permeability/Selectivity Upper Bounds of Membrane-Based Air and Hydrogen Separations, Acs Macro Lett 4 (2015) 947-951. https://doi.org/10.1021/acsmacrolett.5b00512
[110] L.P. Chen, Q. Hui, C.L. Wang, X.Q. Jiang, Molecular simulation on the transport properties of poly 1-trimethylsilyl-1-propyne for organic-vapor/permanent-gas separation, Fluid Phase Equilib. 310 (2011) 142-149. https://doi.org/10.1016/j.fluid.2011.08.001
[111] A. Fuoco, C. Rizzuto, E. Tocci, M. Monteleone, E. Esposito, P.M. Budd, M. Carta, B. Comesaña-Gándara, N.B. McKeown, J.C. Jansen, The origin of size-selective gas transport through polymers of intrinsic microporosity, J Mater Chem A 7 (2019) 20121-20126. https://doi.org/10.1039/C9TA07159H
[112] A. Fuoco, B. Comesana-Gandara, M. Longo, E. Esposito, M. Monteleone, I. Rose, C.G. Bezzu, M. Carta, N.B. McKeown, J.C. Jansen, Temperature Dependence of Gas Permeation and Diffusion in Triptycene-Based Ultrapermeable Polymers of Intrinsic Microporosity, Acs Appl Mater Inter 10 (2018) 36475-36482. https://doi.org/10.1021/acsami.8b13634
[113] A. Kolodziej, S.D. Ahn, M. Carta, R. Malpass-Evans, N.B. McKeown, R.S.L. Chapman, S.D. Bull, F. Marken, Electrocatalytic Carbohydrate Oxidation with 4-Benzoyloxy-TEMPO Heterogenised in a Polymer of Intrinsic Microporosity, Electrochim. Acta 160 (2015) 195-201. https://doi.org/10.1016/j.electacta.2015.01.106
[114] V. Ganesan, E. Madrid, R. Malpass-Evans, M. Carta, N.B. McKeown, F. Marken, Biphasic Voltammetry and Spectroelectrochemistry in Polymer of Intrinsic Microporosity—4-(3-Phenylpropyl)-Pyridine Organogel/Aqueous Electrolyte Systems: Reactivity of MnPc Versus MnTPP, Electrocatalysis-Us 10 (2019) 295-304. https://doi.org/10.1007/s12678-018-0497-8
[115] Y. Rong, R. Malpass-Evans, M. Carta, N.B. McKeown, G.A. Attard, F. Marken, High density heterogenisation of molecular electrocatalysts in a rigid intrinsically microporous polymer, Electrochem. Commun. 46 (2014) 26-29. https://doi.org/10.1016/j.elecom2014.06.005
[116] B. Riza Putra, M. Carta, R. Malpass-Evans, N.B. McKeown, F. Marken, Potassium cation induced ionic diode blocking for a polymer of intrinsic microporosity | nafion "heterojunction" on a microhole substrate, Electrochim. Acta 258 (2017) 807-813. https://doi.org/10.1016/j.electacta.2017.11.130
[117] C. Li, A.L. Ward, S.E. Doris, T.A. Pascal, D. Prendergast, B.A. Helms, Polysulfide-Blocking Microporous Polymer Membrane Tailored for Hybrid Li-Sulfur Flow Batteries, Nano Lett. 15 (2015) 5724-5729. https://doi.org/10.1021/acs.nanolett.5b02078
[118] S.E. Doris, A.L. Ward, A. Baskin, P.D. Frischmann, N. Gavvalapalli, E. Chenard, C.S. Sevov, D. Prendergast, J.S. Moore, B.A. Helms, Macromolecular Design Strategies for Preventing Active-Material Crossover in Non-Aqueous All-Organic Redox-Flow Batteries, Angew Chem Int Edit 56 (2017) 1595-1599. https://doi.org/10.1002/anie.201610582

[119] A.L. Ward, S.E. Doris, L.J. Li, M.A. Hughes, X.H. Qu, K.A. Persson, B.A. Helms, Materials Genomics Screens for Adaptive Ion Transport Behavior by Redox-Switchable Microporous Polymer Membranes in Lithium-Sulfur Batteries, Acs Central Sci 3 (2017) 399-406. https://doi.org/10.1021/acscentsci.7b00012

[120] M.J. Baran, M.N. Braten, S. Sahu, A. Baskin, S.M. Meckler, L. Li, L. Maserati, M.E. Carrington, Y.-M. Chiang, D. Prendergast, B.A. Helms, Design Rules for Membranes from Polymers of Intrinsic Microporosity for Crossover-free Aqueous Electrochemical Devices, Joule 3 (2019) 2968-2985. https://doi.org/10.1016/j.joule.2019.08.025

[121] L. Ma, C. Fu, L. Li, K.S. Mayilvahanan, T. Watkins, B.R. Perdue, K.R. Zavadil, B.A. Helms, Nanoporous Polymer Films with a High Cation Transference Number Stabilize Lithium Metal Anodes in Light-Weight Batteries for Electrified Transportation, Nano Lett. 19 (2019) 1387-1394. https://doi.org/10.1021/acs.nanolett.8b05101

[122] R. Tan, A.Q. Wang, R. Malpass-Evans, R. Williams, E.W. Zhao, T. Liu, C.C. Ye, X.Q. Zhou, B.P. Darwich, Z.Y. Fan, L. Turcani, E. Jackson, L.J. Chen, S.Y. Chong, T. Li, K.E. Jelfs, A.I. Cooper, N.P. Brandon, C.P. Grey, N.B. McKeown, Q.L. Song, Hydrophilic microporous membranes for selective ion separation and flow-battery energy storage, Nat Mater 19 (2020) 195-202. https://doi.org/10.1038/s41563-019-0593-z